



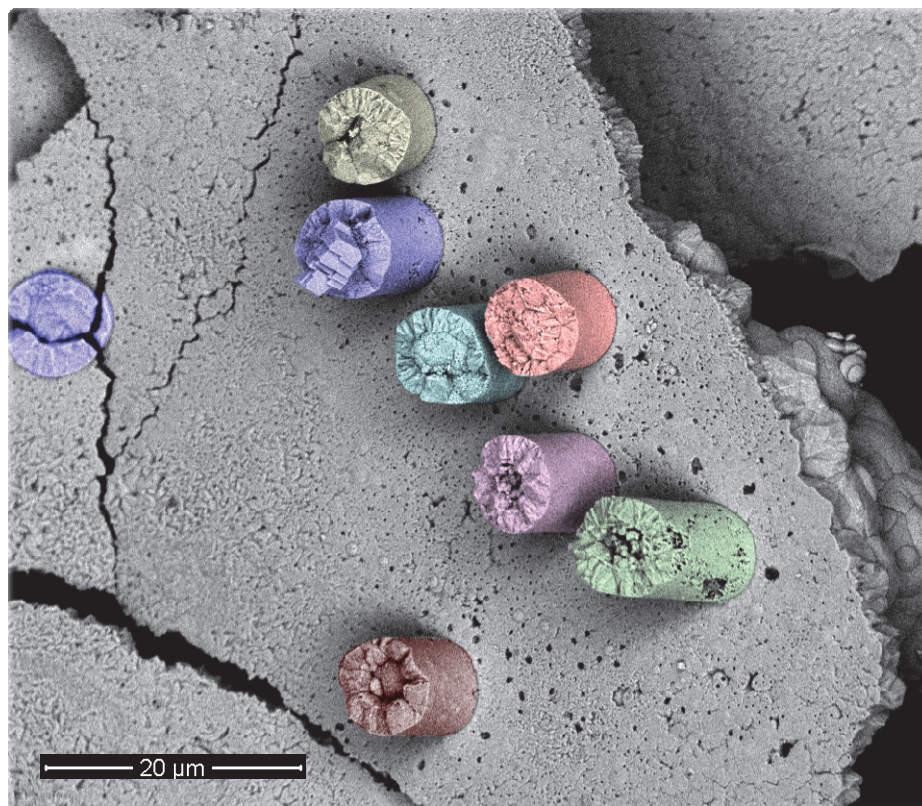
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Electromigration and Deposition of Micro-Scale Calcium Carbonate Structures with Controlled Morphology and Polymorphism

Paul G. Allison, Robert D. Moser, Mei Q. Chandler,
Omar L. Rodriguez, Philip G. Malone, and Charles A. Weiss, Jr.

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Final report

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Abstract

Electromigration and electrodeposition techniques are ideal for synthesizing biomimetic and bio-inspired materials in predefined porous templates. This report demonstrates the utility of precipitating various polymorphs of calcium carbonate in three-dimensional templates. Applied potentials and times were varied and scanning electron microscopy and X-ray diffraction were used to determine polymorph formed and its morphology. It was found that higher applied potentials and shorter operating times resulted in the formation of metastable polymorphs of calcium carbonate (e.g., vaterite) that infilled the porous media. Results are essential for developing bio-inspired composite materials for various structural and medical applications.

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Preface

This study was conducted for the Center Directed Research Program, under Project Number, 6430DL, “Design and Synthesis of Bio-Inspired Nanocomposites.” The technical monitors were Dr. Jeffery P. Holland and Dr. John M. Cullinane.

The work was performed by the Concrete and Materials Branch (GM-C) of the Engineering Systems and Materials Division (GM) and Structural Mechanics Branch (GS-M) of the Geosciences and Structures Division (GS), US Army Engineer Research and Development Center – Geotechnical and Structures Laboratory (ERDC-GSL).

At the time of publication, Christopher Moore was Chief, Concrete and Materials Branch; Dr. Will McMahon was Chief, Structural Mechanics Branch; Dr. Larry N. Lynch was Chief, Engineering Systems and Materials Division; Bart P. Durst was Chief, Geosciences and Structures Division; and Dr. David Horner was the Technical Director for Military Engineering. The Deputy Director of GSL was Dr. William P. Grogan, and the Director was Dr. David W. Pittman.

COL Kevin J. Wilson was ERDC Commander, and Dr. Jeffery P. Holland was the Director.

1 Introduction

Electromigration techniques are gaining increasing consideration as a material processing method. This interest is based not only on its high versatility, as it can be used with different materials and/or combinations of materials, but also because it is a cost-effective technique usually requiring simple processing equipment and laboratory techniques (Boccaccini et al. 2010). In techniques such as electrophoresis and electroplating, the potential differences act as the driving force for the movement of ions or particles suspended in a solution, driving them towards a charged surface or through a porous membrane or material.

Numerous applications investigating the utility of electromigration techniques have been explored including coatings, laminated or graded materials, and infiltration in porous templates (Bersa and Liu 2007). When used as a coating deposition technique, materials can be added to a surface to produce specific enhanced properties (Boccaccini and Zhitomirsky 2002; Sarkar and Nicholson 1996; and Van der Biest and Vandeperre 1999). For example, the application of electrophoresis can be used to produce surfaces with improved wear and oxidation resistance or bio-active coatings for biomedical implants and functional coatings for electronic, magnetic and related applications (Corni et al. 2008).

Morefield et al. (2008), Ma et al. (2003), and Chen et al. (1999) described the use of an electromigration system to infiltrate ions or particles into a porous template for structural, tissue engineering, and microfiltering applications. The success of the electromigration procedures in coating deposition of layered composites and infiltration of porous media has demonstrated that this approach can be a suitable synthesis technique for structural related composites. Of particular interest is the development of bio-inspired composites that can be synthesized using electromigration techniques in 3-D templates.

The research reported here presents techniques for electromigration and precipitation of calcium carbonate in structured templates including microporous polycarbonate membranes and polyethylene foams. Parameters related to the electromigration process and their effects on the mineral phase and morphology were investigated, including applied cell

potential and test duration. The resulting mineral/polymeric composites have potential applications in bio-inspired materials for structural and biomedical applications. Further applications include infilling of templates with a mineral phase such as the synthesis of artificial bone.

2 Experimental

Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, and calcium acetate, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, were used as the reactants for the calcium carbonate (CaCO_3) precipitation that was produced by using electromigration between two solutions separated by a porous template (polycarbonate membrane or polyethylene foam). Microporous polycarbonate membranes and Medium-Density PolyEthylene (MDPE) foam specimens were used as the porous organic templates. Commercial filter holders were modified to produce two reagent reservoirs separated by a disc made from the porous organic medium sealed across the interface between the reactants. Carbon electrodes were used to make electrical contact with the solutions in the reagent reservoirs and a low-voltage electrical power supply was used to produce a potential across the membrane. The kinetics of the electromigration-precipitation process were investigated by varying the potential difference across the membrane and the time the potential was applied across the membrane. The morphology and structure of the electrodeposited crystallites were investigated using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) techniques.

2.1 Materials

Solutions were prepared from analytical grade $(\text{NH}_4)_2\text{CO}_3$ and $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ at concentrations of 0.5-M in deionized H_2O . Each 0.5-M solution of reactants was prepared at room temperature (25°C) with constant stirring until all reagents were fully solubilized.

Nuclepore polycarbonate membranes (47-mm diameter, $\approx 22\text{-}\mu\text{m}$ thickness) and MDPE foam (39-mm diameter, 5-mm thickness) specimens were used as the porous templates. Both template materials are non-conductive substrates. SEM micrographs were used in conjunction with image analysis software (ImageJ) to determine the average pore diameter and density (pores/area) of the polycarbonate films. The calculated average pore diameter for the polycarbonate membranes was $8.81\text{ }\mu\text{m} \pm 1.43\text{ }\mu\text{m}$, which is in accordance with the value reported by the manufacturer (8- μm pore diameter). The average pore density was 900 pores/ mm^2 , and the pore area to film area ratio was 5.47 percent. The MDPE foam specimen was measured using the ASTM C642-06 (ASTM 2006) standard as a reference criterion to determine the void space volume fraction.

2.2 Electromigration experimental setup

A commercial Nalgene® MF-75 series filter holder unit acted as the electromigration cell. Each unit included two fluid reservoirs (500 ml each) in which the CaCO_3 forming reagents were deposited; the porous template served as the interface between them. Whatman® membranes were accommodated on the holder's analytical support plate, and the MDPE foam samples were plugged onto a support plate replacement collar. The chamber cover, supporting plate, replacement collar O-rings, and MDPE foam specimen circumference were grease-sealed. Acrylic bases were custom made to maintain the Nalgene® filter holder in a horizontal position.

Graphite electrodes were used to apply voltage across the cell. The anode was located in the $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution chamber, and the cathode was positioned in the $(\text{NH}_4)_2\text{CO}_3$ chamber. Both electrodes were placed at 70.0 mm distance from a porous template. A schematic of the experimental setup is presented in Figure 1.

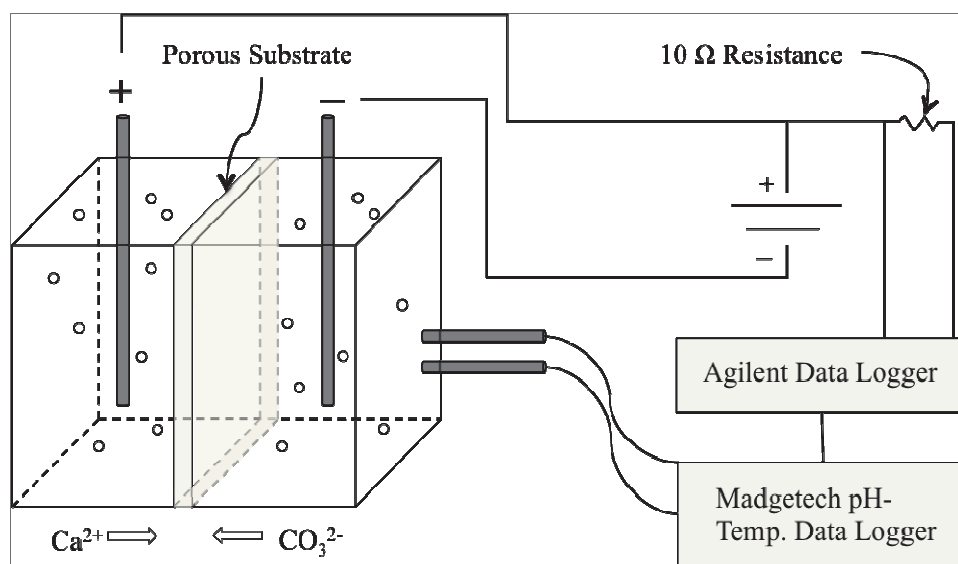


Figure 1. Electromigration cell experimental setup schematic.

A regulated power supply delivered a constant voltage to each Nalgene® station. For the polycarbonate membranes, a cell potential of 5.0, 10.0, and 20.0 volts was applied with testing durations of 2-, 3-, and 6-hr. Experimental conditions of 10.0, 20.0, and 30.0 volts, with duration periods of 2-, 6-, or 12-hr were applied to the MDPE foam samples. At the end of the deposition time, the specimens were extracted from the electromigration cell with tweezers and let dry at 25° C for 48 hr.

An Agilent data acquisition unit recorded the voltage across a 10- Ω resistor. Agilent BenchLink Data Logger software was employed to generate voltage time plots. A Madgetech® data logger collected solution temperature and pH data. Both meters were positioned on the $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution chamber.

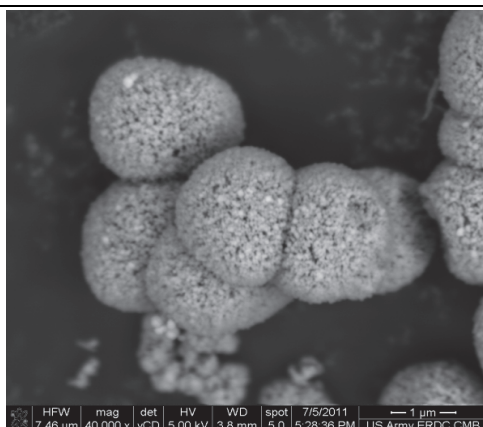
2.3 Characterization techniques

An FEI Nova NanoSEM 630 environmental Scanning Electron Microscope (SEM) was used to investigate the morphology of the specimens. The specimens were analyzed using a backscattered electron detector (vCD). Accelerating voltages ranged from 5- to 15-kV. X-ray diffraction patterns for the specimens were obtained using a PANalytical X'pert powder diffractometer (Co anode) operating at a voltage of 45-kV and current of 40-mA. Data was collected at a 2θ deg angle ranging from 2-deg-70-deg. The specimens were positioned above zero background plates and covered with Kapton films. X'pert High Score Plus and MDI Jade 2010 analysis software, with access to ICDD reference databases, were used for qualitative phase identification.

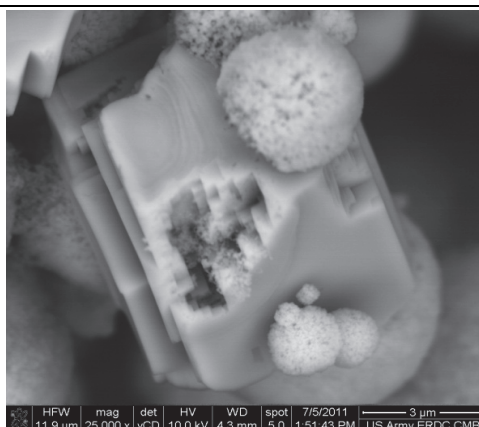
3 Results and Discussion

3.1 Morphology of electrodeposited CaCO_3

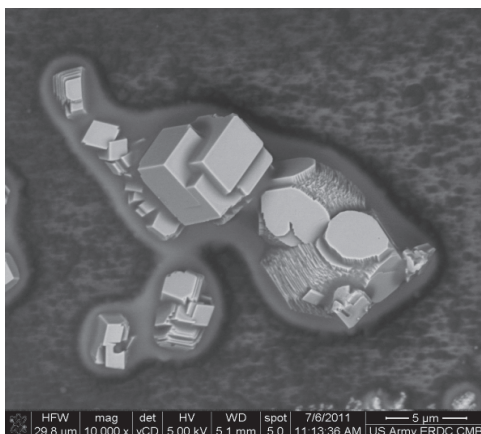
Electrodeposited precipitates of CaCO_3 resulting from electromigration between calcium acetate and ammonium carbonate solutions were primarily botryoidal agglomerates of vaterite nanoparticles (Figure 2a), larger rhombohedral formations of calcite (Figure 2b), or amorphous calcium carbonate (Figure 2c). More stable polymorphs (i.e., calcite) formed via Ostwald ripening from less stable forms like vaterite and amorphous calcium carbonate (Figures 2b and 2c). The following sections describe the deposition of these into polycarbonate membranes and polyethylene foams and the effect of cell potential and time on observed crystal morphology.



(a) Botryoidal agglomerations of vaterite nanoparticles.



(b) Transformation of vaterite nanoparticles into calcite rhombs.



(c) Transformation of amorphous calcium carbonate to calcite rhombs.

Figure 2. Polymorphism observed in electrodeposited precipitates of CaCO_3 .

3.2 Electromigration and P\precipitation of CaCO_3 in polycarbonate membranes

The relationship between cell current (on a logarithmic scale) and duration of applied cell potentials of 5-, 10-, and 20-V is shown in Figure 3. Additional sensors monitored during the test confirmed a constant temperature of 24° C and pH of 8.8 to 9.0. Initial currents roughly corresponded to the magnitude of the applied cell potential, with higher cell potentials (e.g., 20-V) yielding higher currents. However, the measured current deviated quickly from this trend as the deposition of CaCO_3 occurred and began to fill the pore spaces in the polycarbonate membrane. This infilling of pores leads to the rapid decrease in current with time and erratic shifts in current as the pores transform from open ionically conductive pathways to filled resistive pathways for ion transport and the deposition of CaCO_3 . This is evidenced by the SEM micrographs, shown in Figure 4, with the originally open pores (Figure 4a) that become filled with various polymorphs of CaCO_3 (Figures 4b and 4c), effectively cutting off ionic connectivity locally between the anodic and cathodic portions of the electromigration cell.

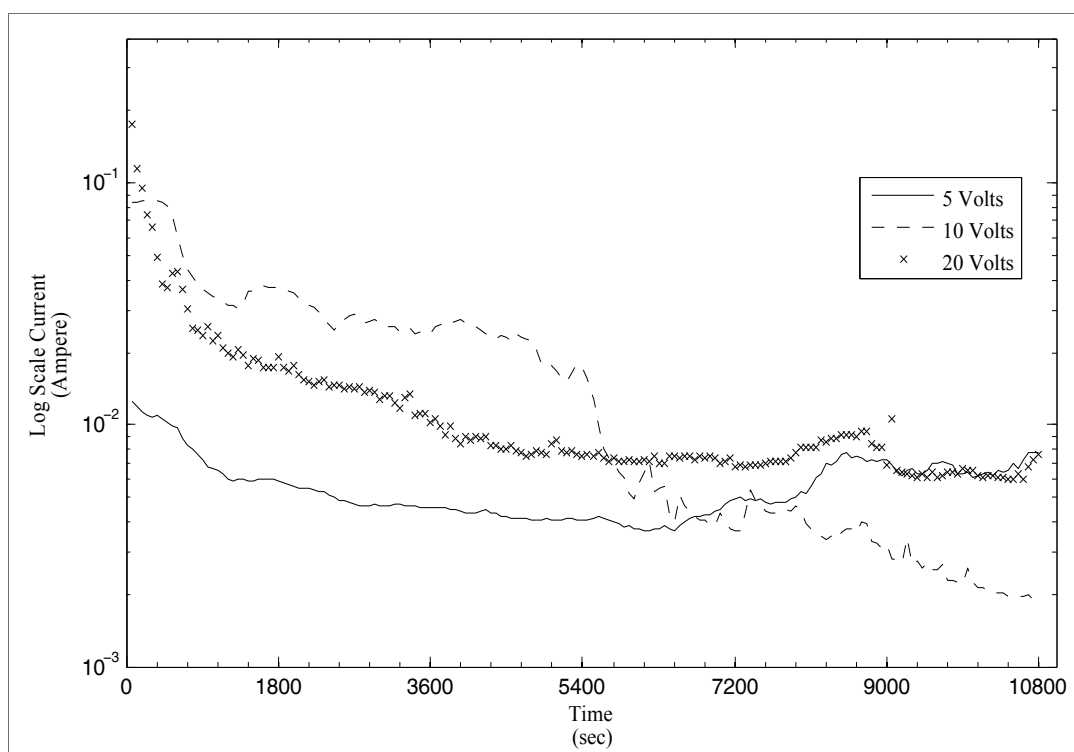


Figure 3. Current versus time relationship for the calcium carbonate deposition process in polycarbonate substrates.

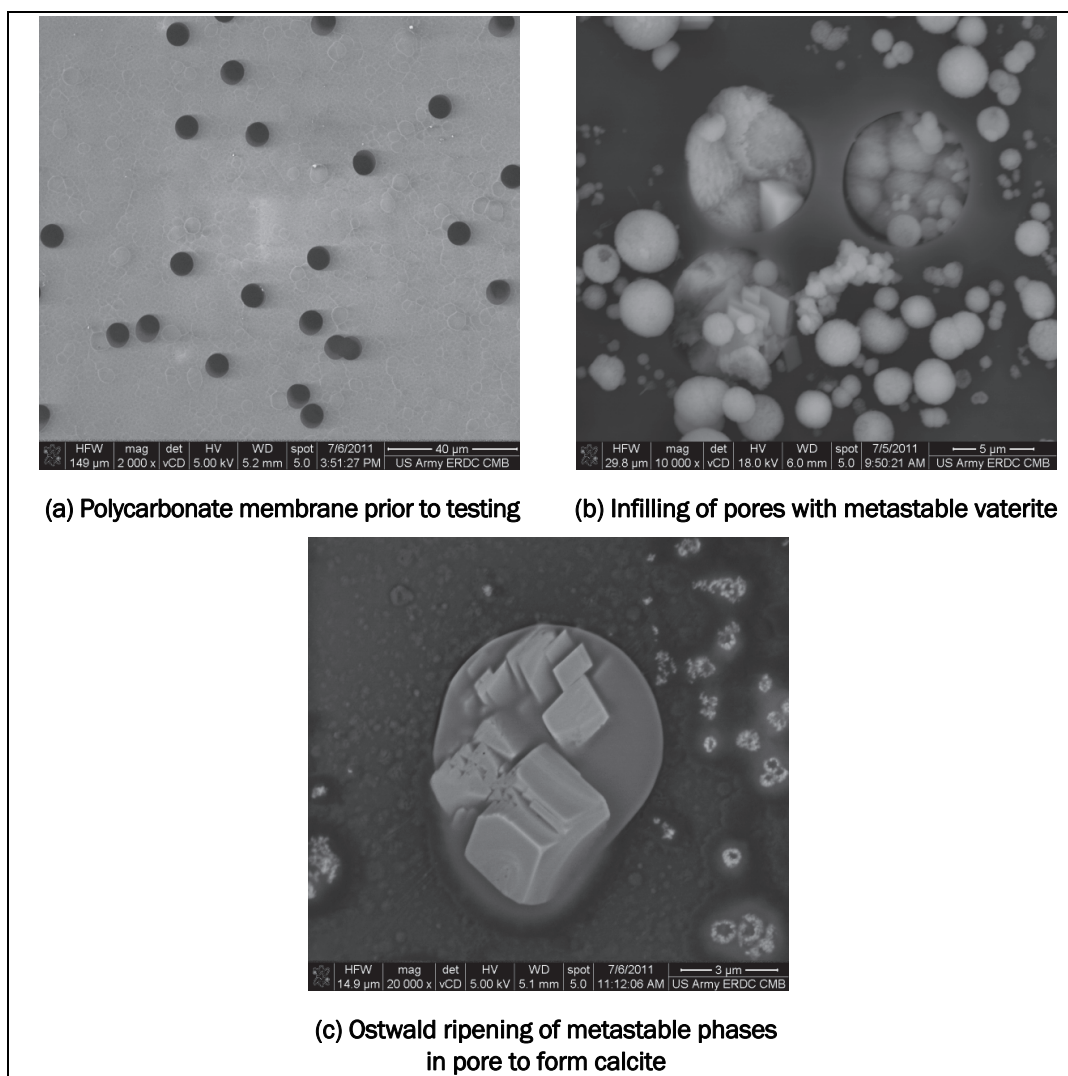


Figure 4. Infilling of pores in polycarbonate membrane.

To quantitatively compare specimens with different cell potential differences, a CaCO_3 saturation criterion was established; that is to say, the current drop at which it was found that all of the pores were infilled with CaCO_3 . When the decaying current curve reached 10 percent of its first measured value, the template was considered saturated. The amount of CaCO_3 precipitated on the polycarbonate membrane was quantitatively determined by mass measurements of pre- and post-deposition specimens. Results of these measurements are presented in Table 1. An increase in mass associated with the formation of CaCO_3 on the membrane surface and infilling of the pores was observed. However, there were no clear trends between amount of CaCO_3 deposited and applied cell potential.

Table 1. Calcium carbonate – polycarbonate specimens weight distribution by applied potential difference. Deposition time: 3 hr.

Cell Potential Difference (Volts)	Mass (g) ¹	Δ Mass % ²
5	0.0348 \pm 0.0071	+ 159.47
10	0.0438 \pm 0.0043	+ 226.58
20	0.0415 \pm 0.0113	+ 209.43

¹ Post-deposition process mass. The values presented are the average of five specimens with standard deviation.

² Compare to the polycarbonate template average mass, 0.0130 \pm 0.0015 grams.

Finally, the influence of applied cell potential and time on CaCO_3 polymorphism was examined. Results of SEM imaging and XRD analyses confirmed that these variables do influence which polymorph of CaCO_3 forms, with metastable vaterite precipitation preferentially under higher applied cell potentials and lower test durations. The XRD patterns presented in Figure 5 demonstrate the increased presence of vaterite at shorter test durations in specimens synthesized with a 10-V applied cell potential.

The XRD patterns in Figure 6 demonstrate the influence of applied cell potential, with the promotion of vaterite formation at 20-V vs. 0-V over a 3-hr test duration. SEM imaging confirmed the trends in crystal polymorph formed (Figure 7). These results demonstrate the utility of using the electromigration and deposition procedure presented herein to promote the formation of specific polymorphs of CaCO_3 and preferentially deposit a mineral phase into a porous template.

3.3 Electromigration and precipitation of CaCO_3 in polyethylene foams

In addition to tests performed in a thin polycarbonate membrane, the developed electromigration and precipitation technique was also investigated for infilling of 3-D porous templates such as an MDPE foam. Figure 8 shows representative results of the current vs. deposition time relationship for the MDPE foam specimens. Similar behavior, as in the polycarbonate membranes, was observed in the MDPE foam specimens, with a decrease in current with time as the pore spaces begin to infill with CaCO_3 . The decrease in current was more gradual when compared with the polycarbonate membranes, which is likely due to the larger pore sizes and greater pore interconnectivity, which lessens the propensity for the infilling of pores to block ions through the membrane.

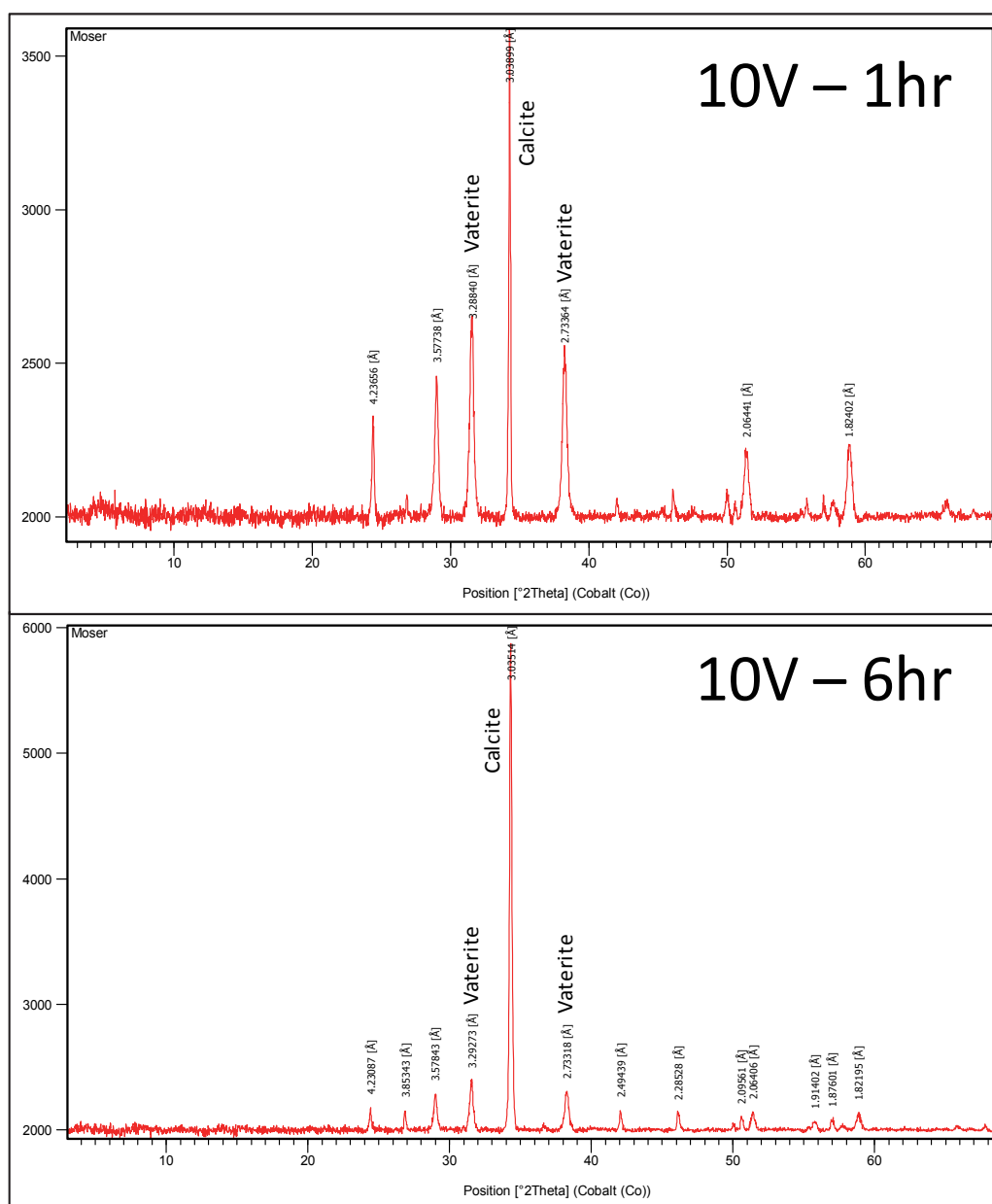


Figure 5. Comparison of CaCO_3 formed under 10-V applied cell potential with testing durations of 1 hr and 6 hr.

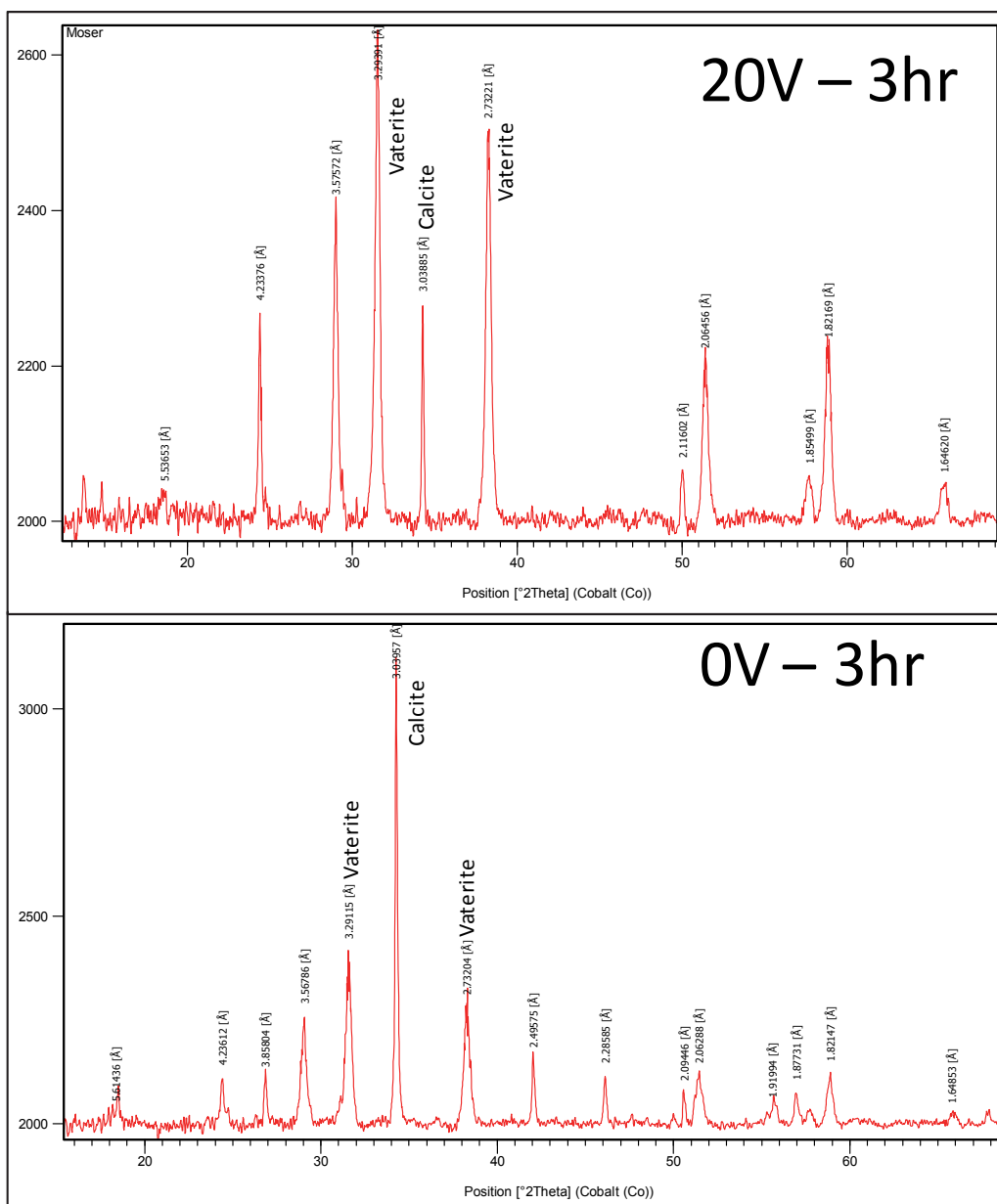


Figure 6. Comparison of CaCO_3 formed under 20-V and 0-V applied cell potential over a 3-hr test duration.

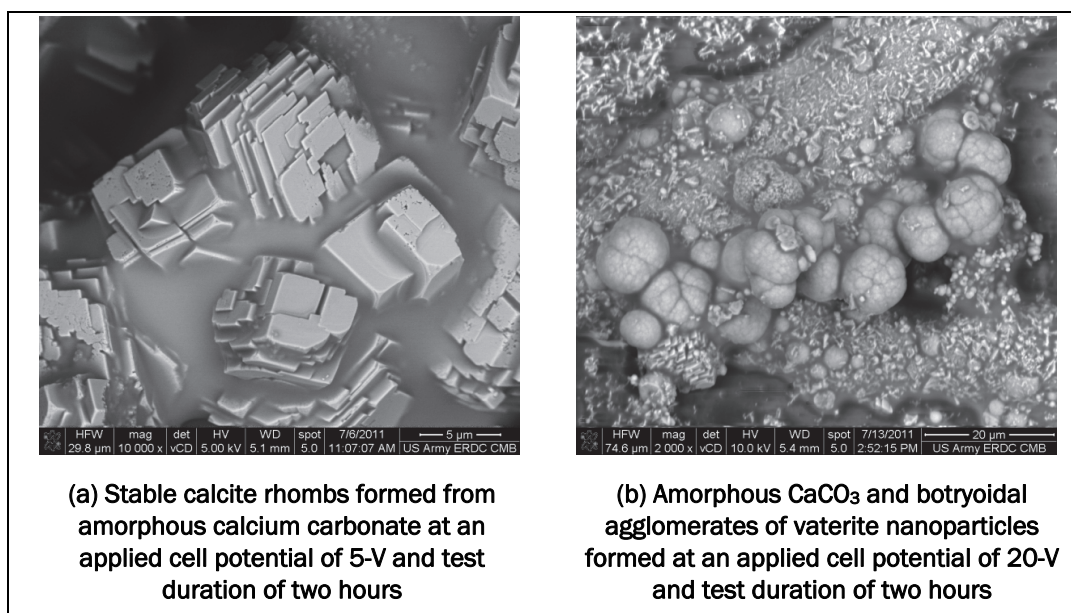


Figure 7. Influence of applied cell potential on CaCO_3 polymorphism.

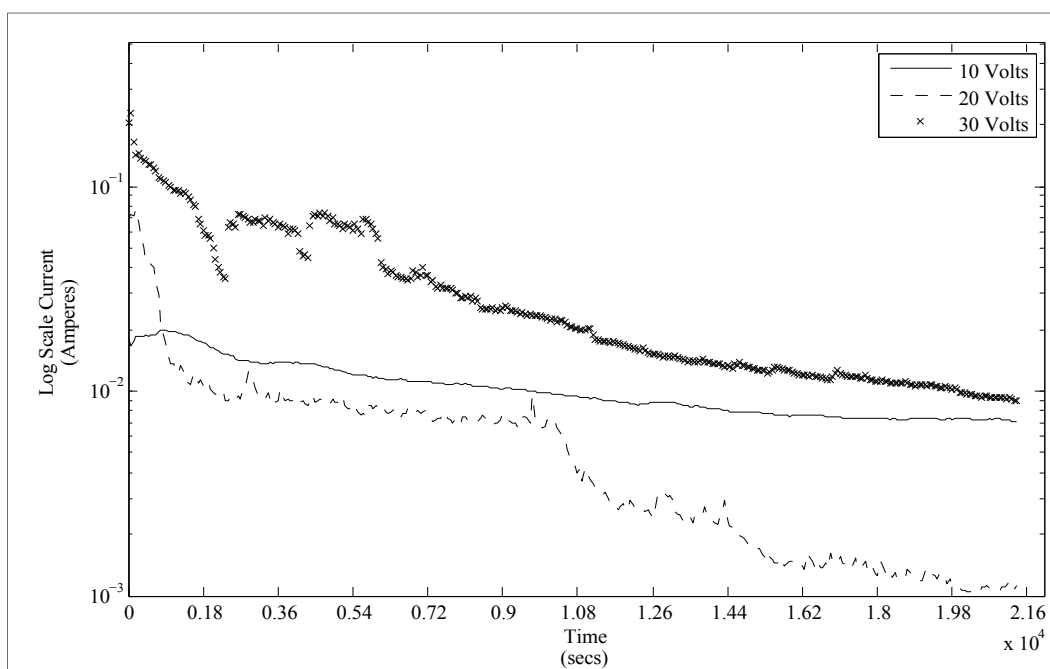


Figure 8. Current – time relationship for the calcium carbonate deposition process in medium density polyethylene foam substrates.

Measurements of mass gain presented in Table 2 demonstrate the increase in mass observed in MDPE foams following testing. However, like the polycarbonate membranes, no clear relationship between applied cell potential and mass gain can be stated. The factors that are influencing the measurements are likely the poor cohesion between CaCO_3 and the MDPE substrate, and the handling of the specimens after the deposition.

Table 2. Calcium carbonate – medium density polyethylene foam samples weight distribution by applied potential difference. Deposition time: 6 hr.

Cell Potential Difference (Volts)	Mass (g) ¹	Δ Mass % ²
10	0.8883 ± 0.0046	+ 37.30
20	0.8237 ± 0.1287	+ 27.32
30	0.9108 ± 0.0811	+ 40.77

¹ Post-deposition process mass. The values presented are the average of five specimens with standard deviation.

² Compare to the medium density polyethylene foam template average mass, 0.6470 ± 0.0670 grams.

SEM imaging of the MDPE foams revealed a partial infilling of the pore spaces with CaCO_3 following the testing duration (Figure 9).

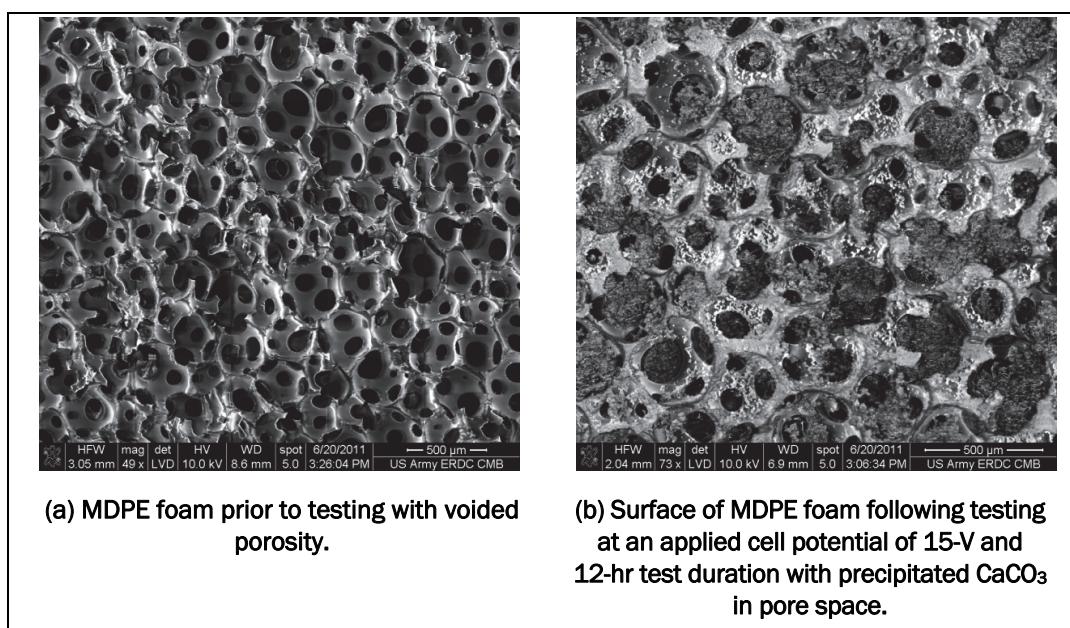


Figure 9. MDPE foam specimen before and after electromigration experiment.

However, infilling was observed to occur preferentially on one side of the electromigration cell, as can be observed in the specimen cross section shown in Figure 10. The thickness of this deposited layer was found to be approximately 300 to 500 μm , which is approximately 10 percent of the total specimen thickness. This result suggests that the increased ionic mobility of Ca^{2+} ions, when compared with CO_3^{2-} , shifts the reaction front to the $(\text{NH})_4\text{CO}_3$ solution side of the electromigration cell. Results from studies of the MDPE foams demonstrated the difficulty of fully infilling a 3-D matrix. As a result, such techniques may be limited to thin coatings or 3-D structures, where infilling of pores does not severely limit subsequent electrodeposition events.

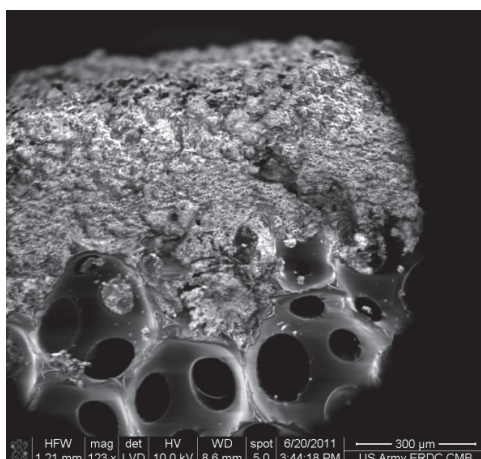


Figure 10. Cross section of MDPE foam specimen showing preferential deposition on carbonate side of electromigration cell.

3.4 Utility for producing predefined 3-D structures

Results of the studies presented herein conducted on polycarbonate membranes and MDPE foams demonstrated the ability to infill a template material with a mineral phase using an electromigration technique between two reactive solutions. Removal of the template material following deposition (e.g., using an appropriate solvent to dissolve the template) reveals 3-D structures that are the negative of the template (see Figure 11). Potential applications for this technique include synthesis of 3-D structures of mineral phases such as CaCO_3 (e.g., biometric materials) or hydroxyapatite (e.g., artificial bone) in predefined templates.

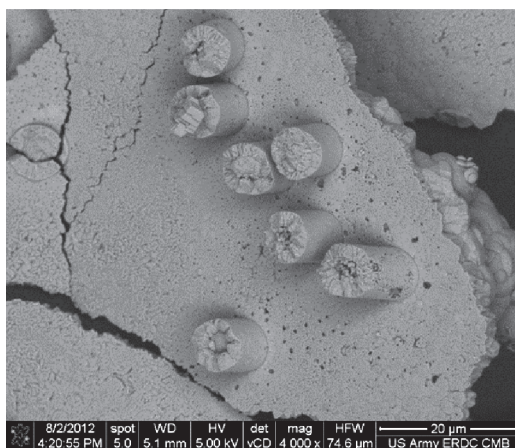


Figure 11. Micropillar of CaCO_3 formed by infilling of polycarbonate membrane and liftoff of membrane to reveal template mineral deposit.

4 Conclusions and Future Work

In this research, the use of electromigration was demonstrated as a method to deposit CaCO_3 in porous materials, including polycarbonate membranes and MDPE foam. Electrodeposited CaCO_3 was characterized using SEM and XRD analyses. The primary conclusions of the study are listed below.

- The use of electromigration to promote the movements of oppositely charged reactive ions toward a reaction front is an effective method to infill porous materials with a mineral phase.
- Higher applied cell potentials and shorter test durations resulted in an increase in the proportion of metastable phases such as vaterite and amorphous calcium carbonate. Lower potentials and longer durations promoted the transformation of metastable phases to stable calcite via Ostwald ripening.
- The electrodeposition process is self-limited by reductions in the ionic conductivity between the anodic and cathodic portions of the electromigration cells, and the individual pores are infilled with the mineral phase.
- Three-dimensional porous materials with increased thickness (i.e., the MDPE foam investigated) present a challenge, in that the location of the anode and cathode and the geometry of the electric field between each electrode must be calculated based on ionic mobility (in this case for Ca^{2+} and CO_3^{2-}) to ensure that the reaction front is within the porous template.
- Extending this electromigration and deposition technique to other porous templates and materials may have many applications in the fields of biomimetic materials, artificial implants, and bone regeneration, where techniques for synthesizing micro- and nano-scale structured mineral phases are needed.
- Future work will focus on extending this technique to other porous templates (e.g., nacre-inspired three-dimensional brick and mortar structures) and investigating other infilling materials such as hydroxyapatite.

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Appendix A: Scanning Electron Micrographs

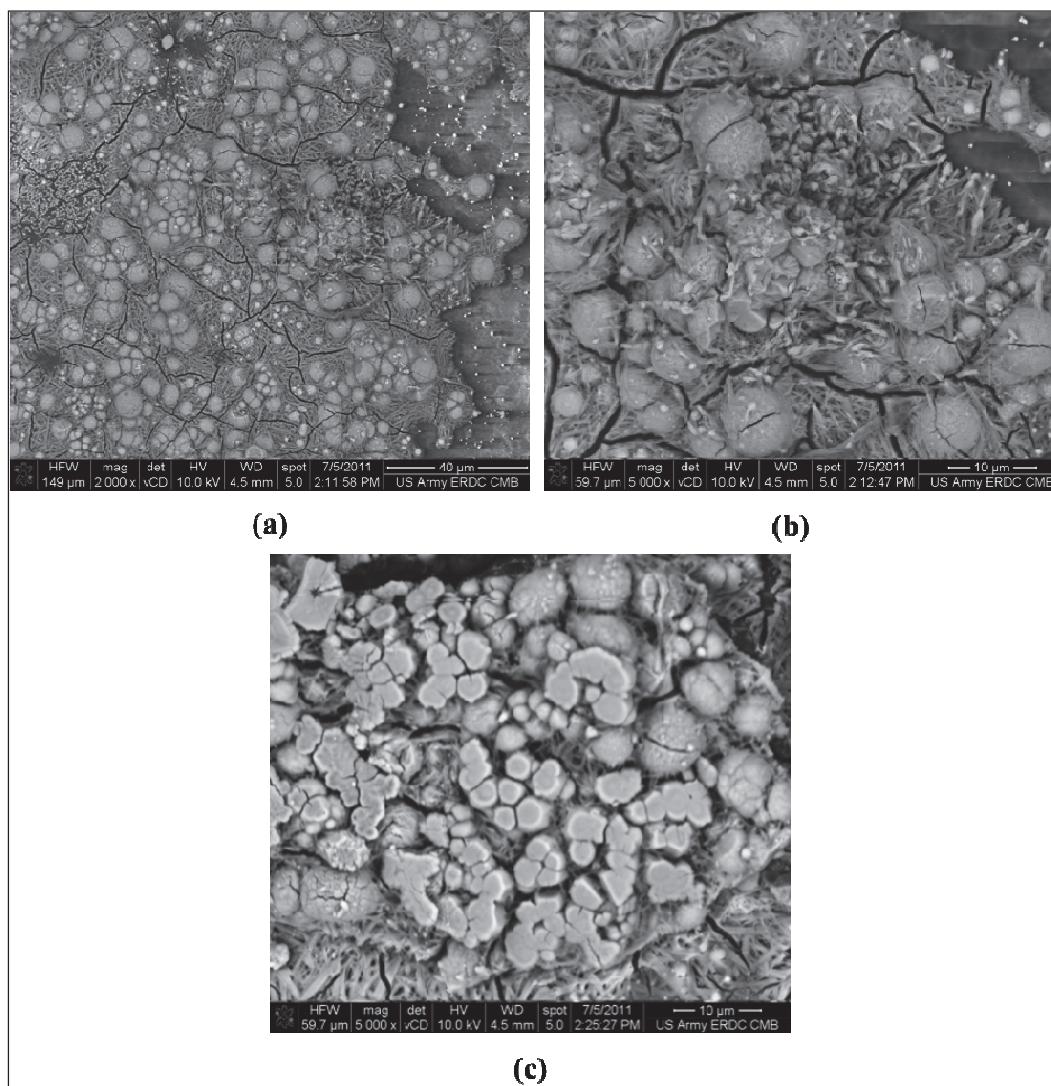


Figure A1. Scanning electron microscopy was employed for the visual inspection of the morphology of the electrodeposited CaCO_3 layer. A polycarbonate membrane acts as the template. (a), (b), and (c) present photomicrographs of a one hr - 10 volt sample.

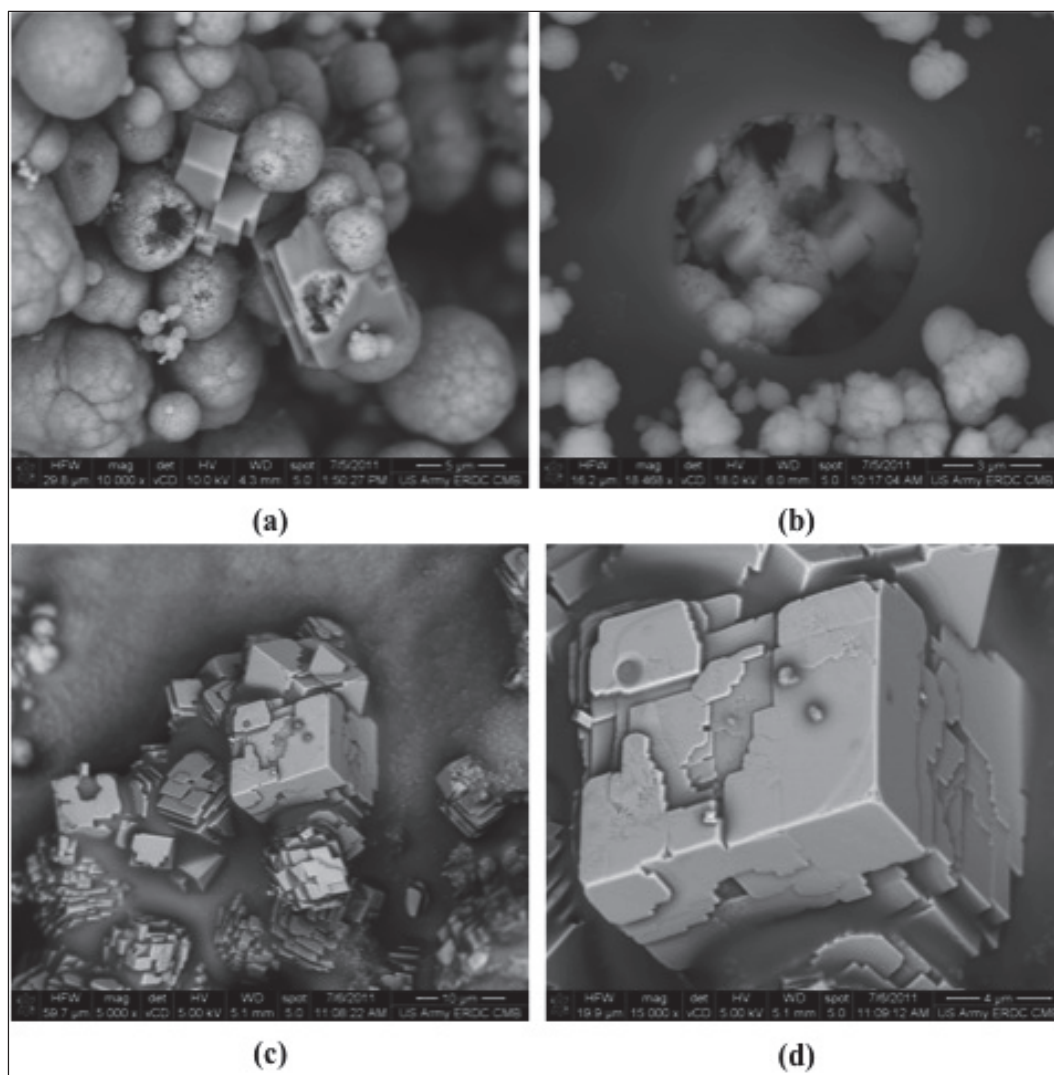


Figure A2. The transformation from vaterite nanoparticles (a) and from amorphous CaCO₃ to calcite rhombs, (c) and (d), can be appreciated. The polycarbonate pores filled with CaCO₃ polymorphs are shown on (b). The micrographs correspond to 5 V–2 hr electrotransport specimens.

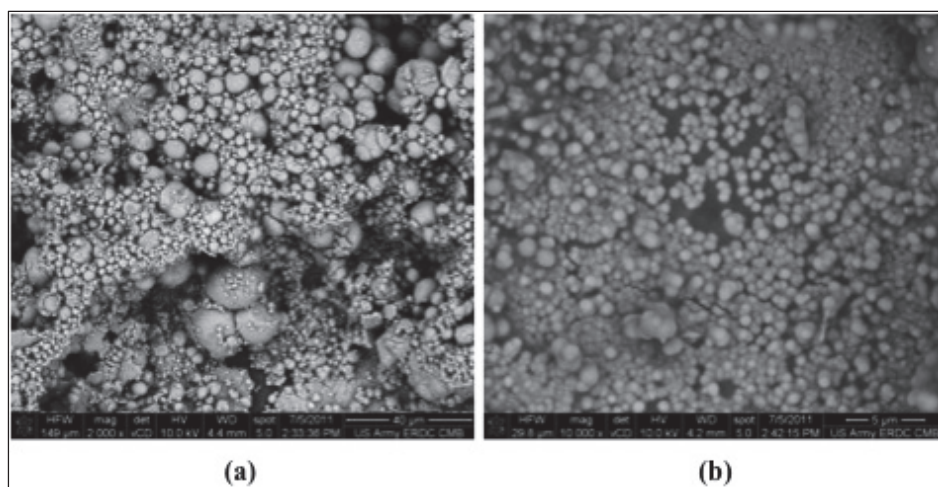


Figure A3. (a) and (b) present a vaterite sphere coating over polycarbonate membrane. The metastable phase was linked to shorter deposition periods. The test duration was two hr with an electric cell potential of 10 V.

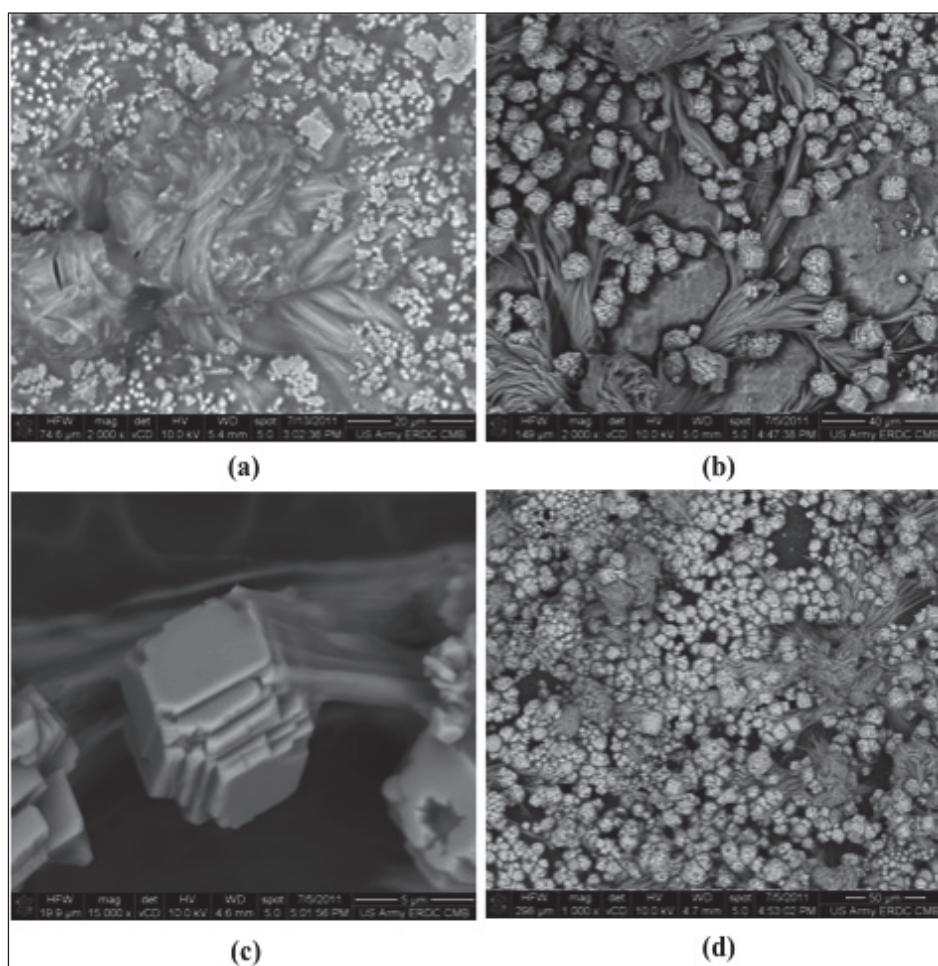


Figure A4. Transformation from metastable amorphous CaCO_3 to stable calcite was observed in the 20-V-2-hr polycarbonate template micrographs.

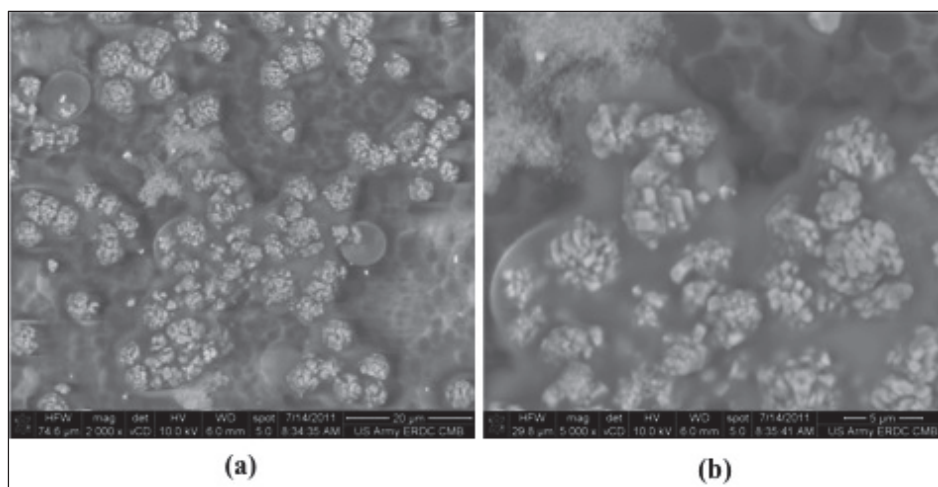


Figure A5. In the absence of an electric potential, diffusion was the only transportation mechanism. As expected, only agglomerates of CaCO_3 were deposited. The micrographs correspond to zero V–3-hr samples.

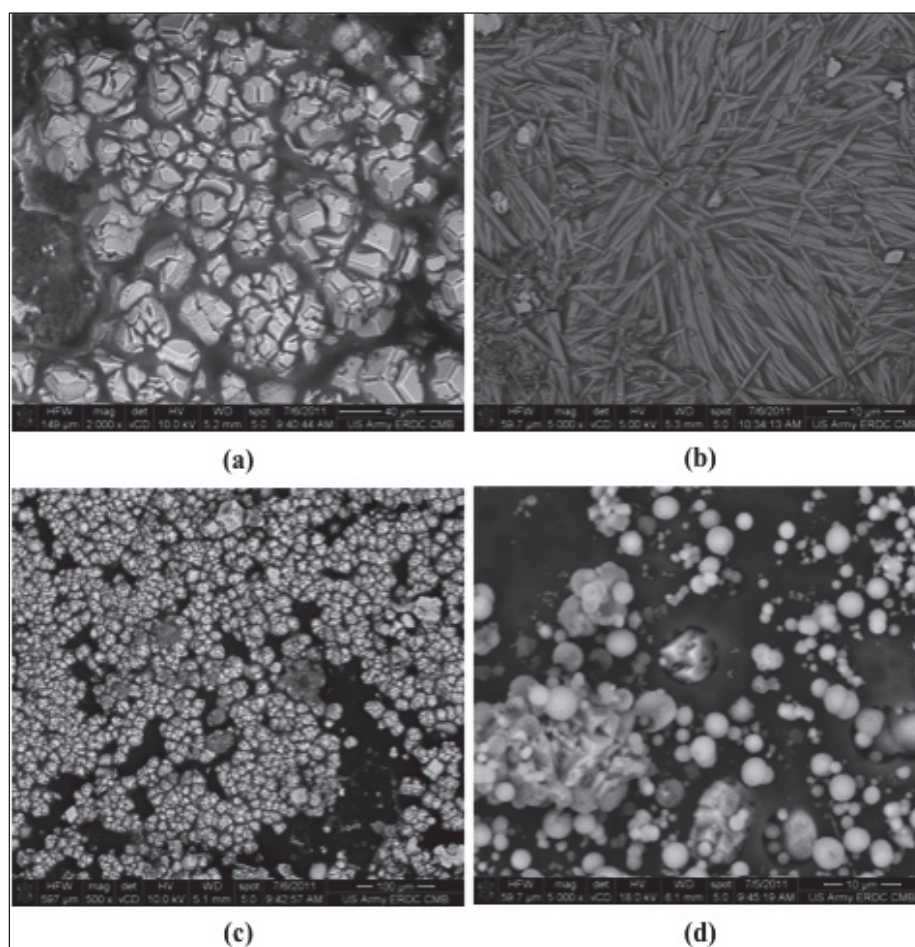


Figure A6. Calcite rhombs (a), aragonite crystals (b), and vaterite to calcite transformation (c), are shown in the micrographs. Infilling polycarbonate pores (d) are responsible for the reduction of the ionic conductivity through the template.

Test duration: three hr with an applied cell potential of five volts.

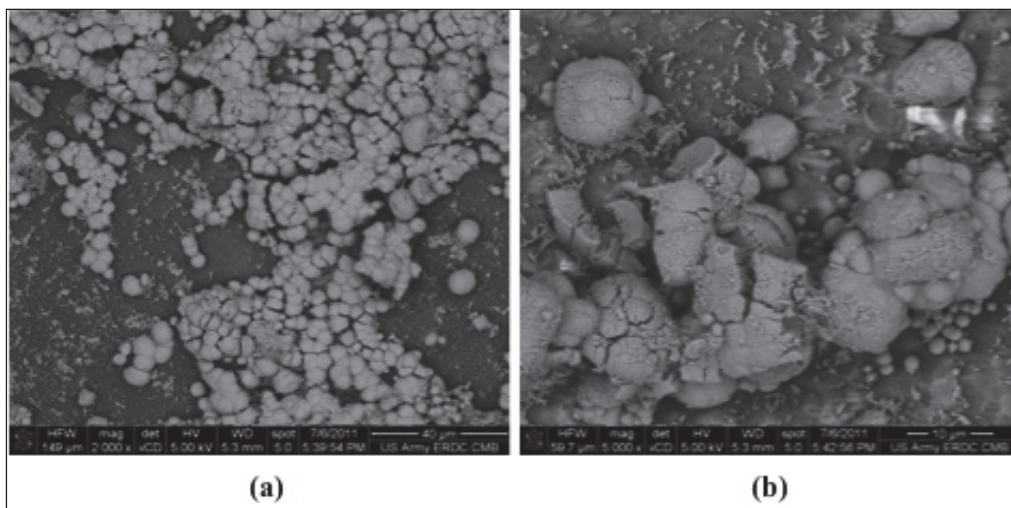


Figure A7. Vaterite agglomerates (a) and (b) are deposited over a polycarbonate membrane. Electrode position time was set to 3 hr with an applied voltage of 10 V.

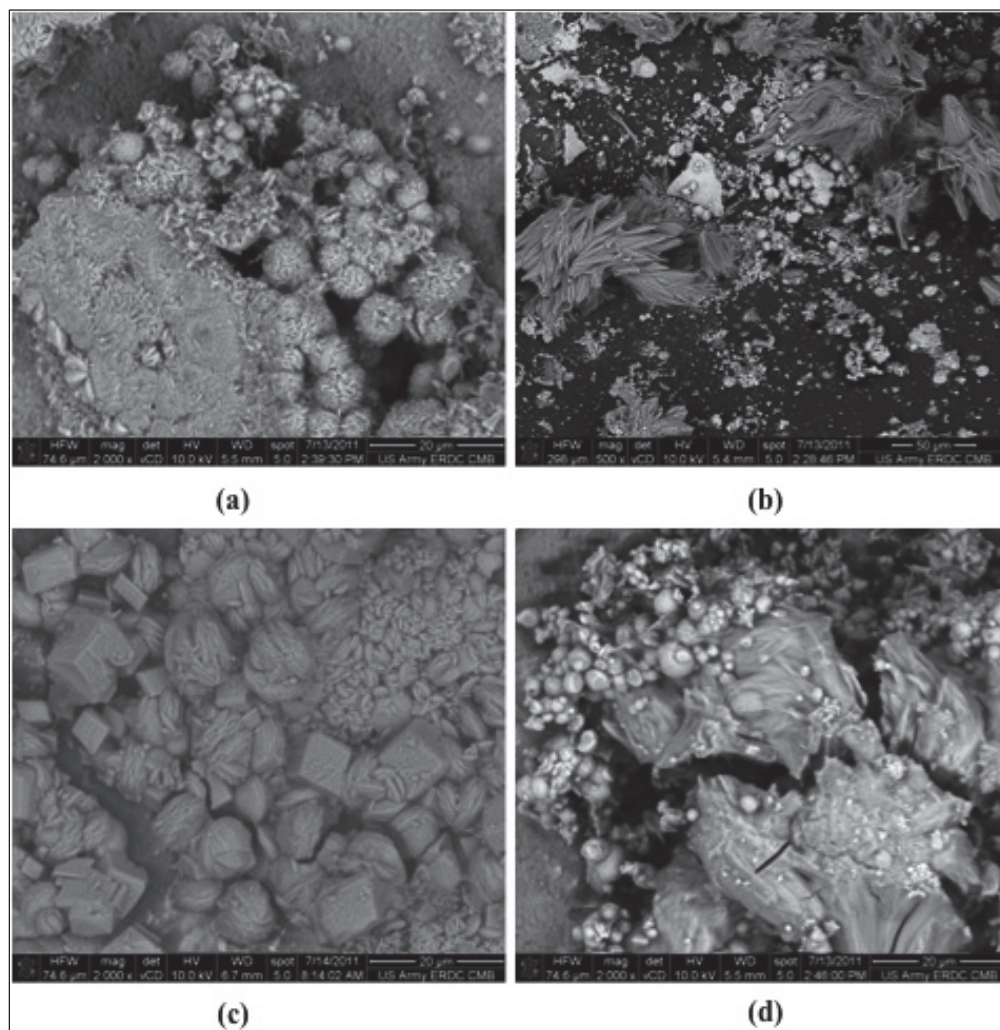


Figure A8. Scanning electron photomicrograph, (a), (b), (c) and (d), of a 3 hr-20 V polycarbonate template specimen.

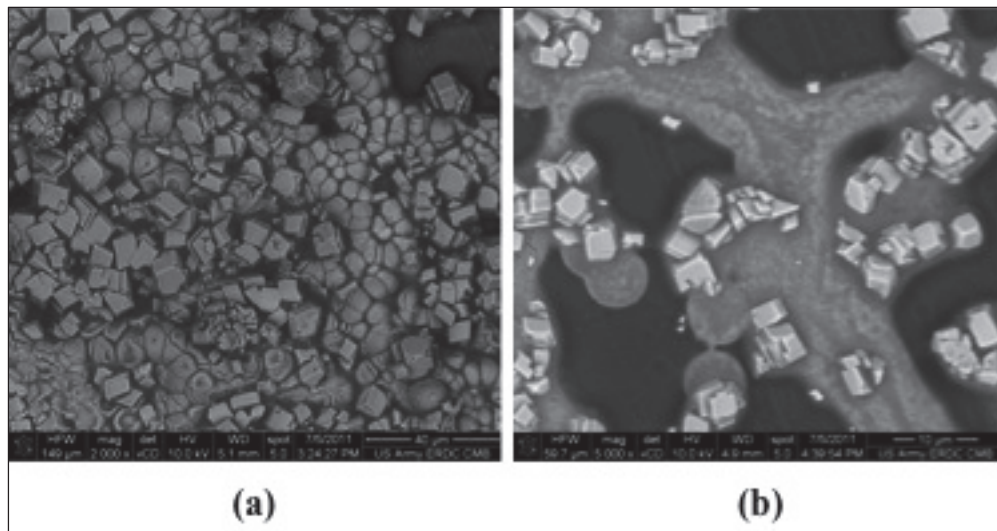


Figure A9. Scanning electron photomicrograph, (a) and (b), of a 6 hr-10 V polycarbonate template specimen.

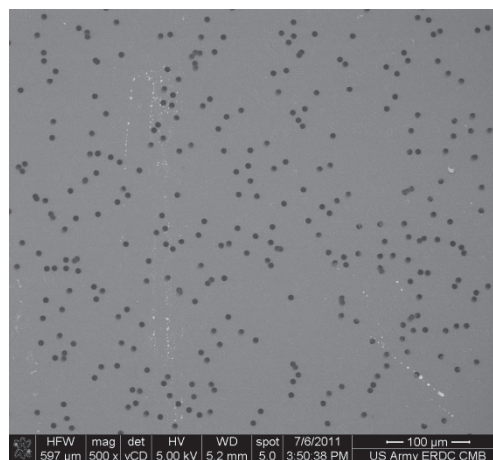


Figure A10. Scanning electron micrograph of a Nuclepore® polycarbonate membrane (47-mm diam, $\approx 22\text{-}\mu\text{m}$ thickness). The calculated average pore diameter for the polycarbonate membranes was $8.81\text{ }\mu\text{m} \pm 1.43\text{ }\mu\text{m}$. The average pore density was 900 pores/ mm^2 , and the pore area to film area ratio was 5.47 percent.

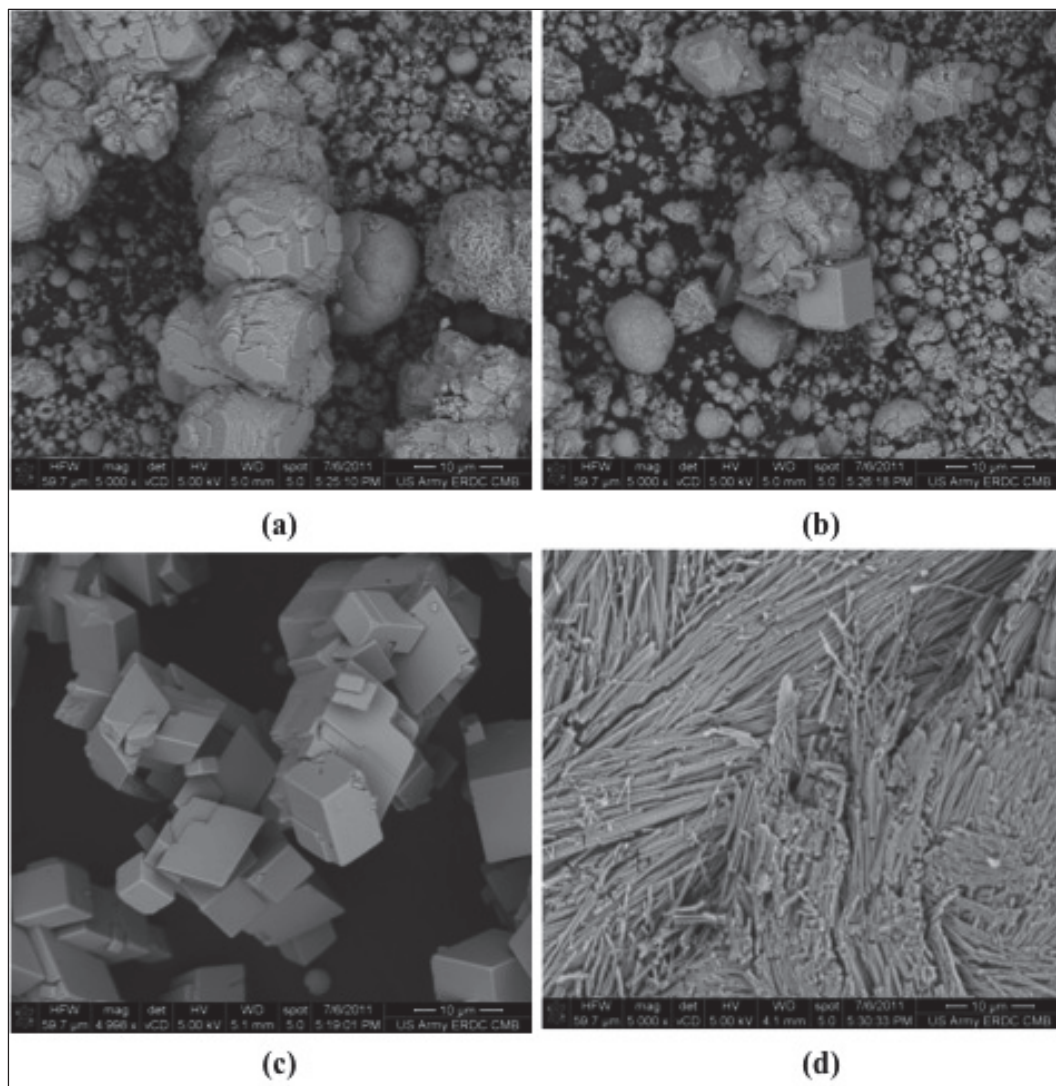


Figure A11. Electrodeposition precipitates left over on the Pyrex® petri dishes used for drying the templates. Micrographs (a) and (b) show the transformation from vaterite spheres to calcite rhombs; meanwhile, figures (c) and (d) present calcite and aragonite polymorphs.

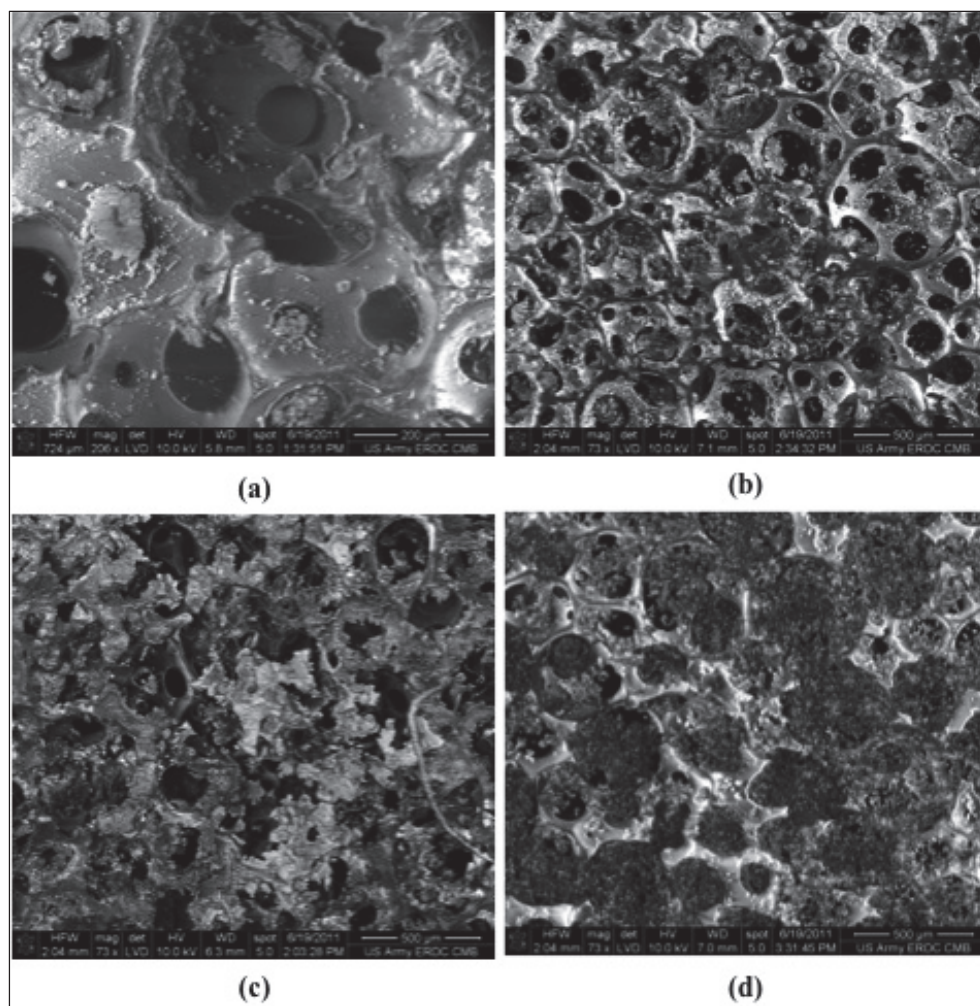


Figure A12. Top views (a), (b), (c) and (d) of an infilled MDPE porous substrate. Duration period: 6 hr, applied voltage: (a) 10 V, (b) 15 V, (c) 20 V and (d) 30 V. Notice the proportional relationship between applied cell potential and filler concentration.

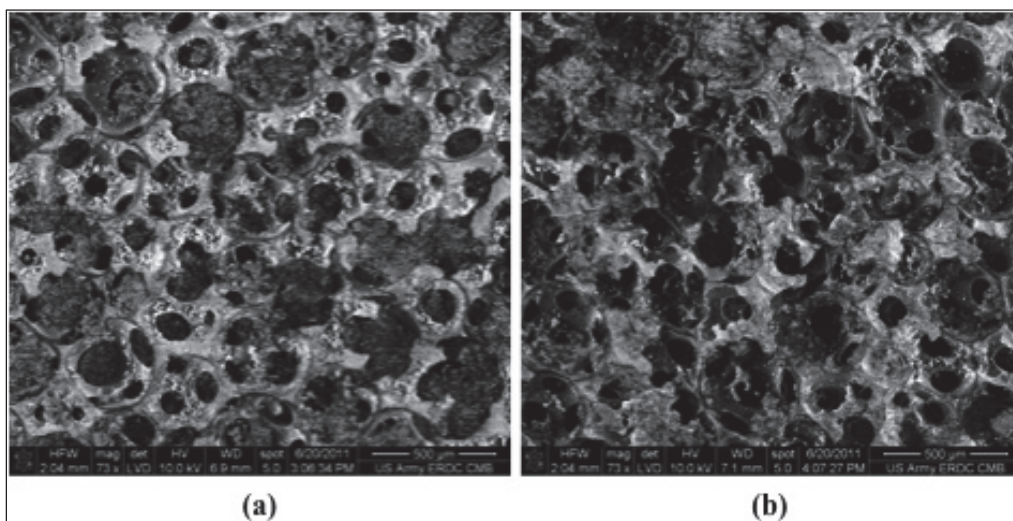


Figure A13. Top view of a 12 hr-15 (a) and 20 V (b) MDPE electrodeposition specimen.

Appendix B: pH and Temperature Data

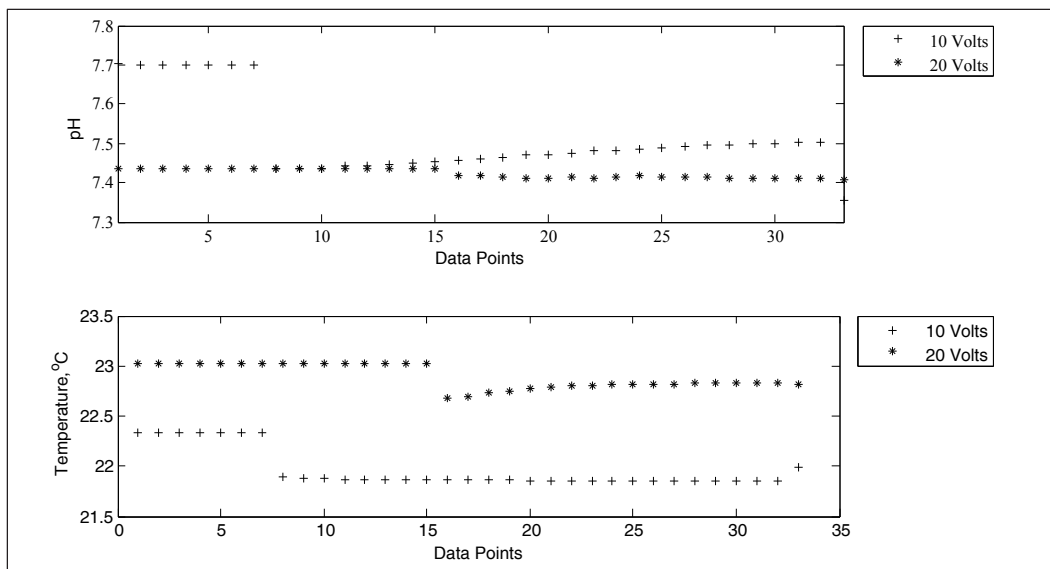


Figure B1. pH and temperature – time relationship for a 2-hr electrodeposition process on a polycarbonate substrate. Notice the constant behavior of variables through the 35 data points reported.

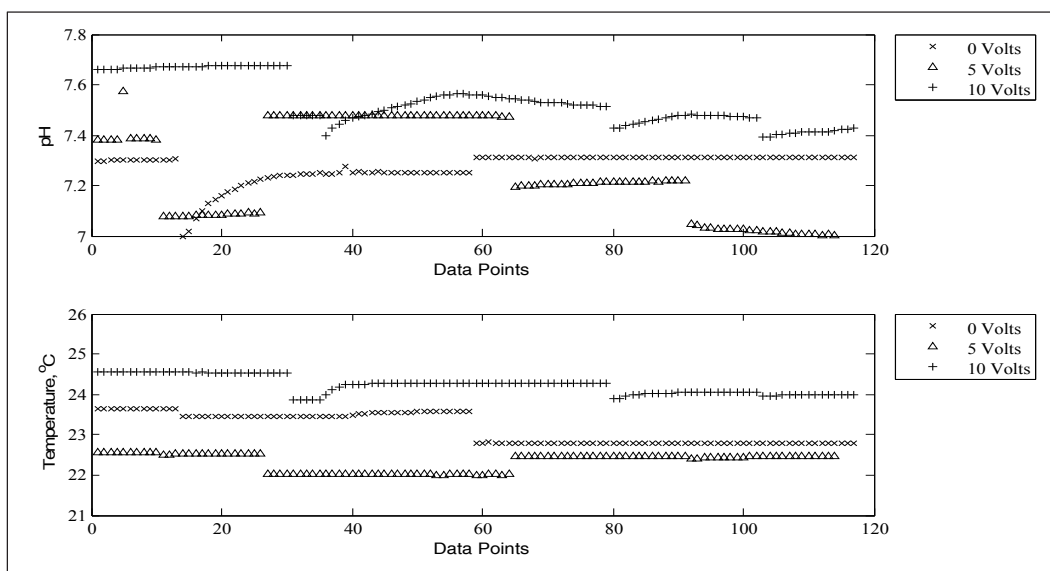


Figure B2. Three-hr pH and temperature data set for 0-, 5- and 10-V specimens. Approximately 120 data points were reported, which are not evenly spaced in the 3-hr course.

Appendix C: Current Data

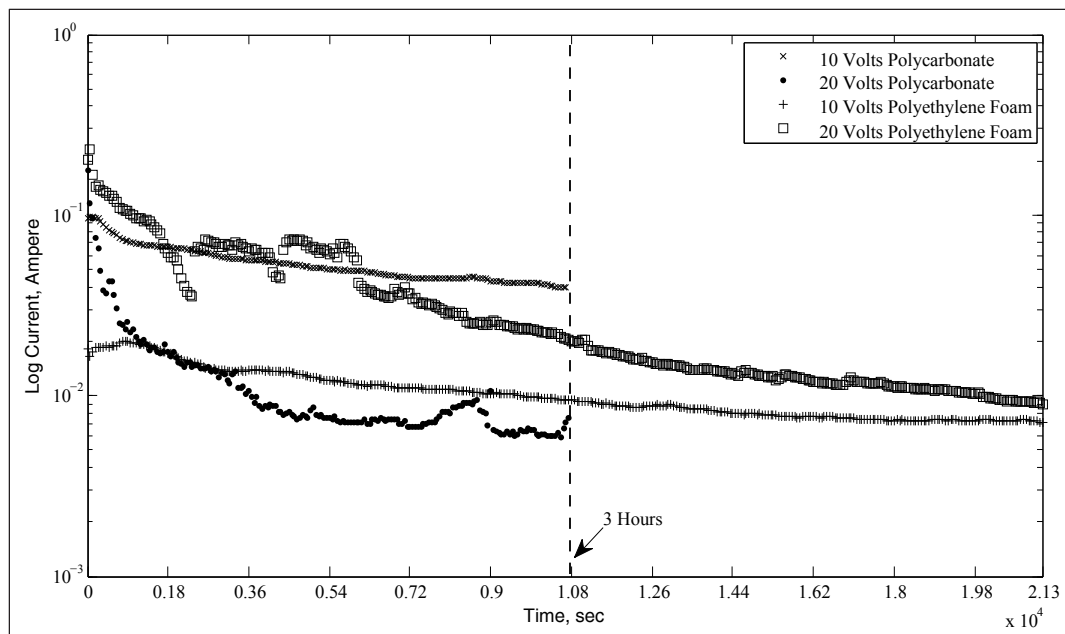


Figure C1. Current versus time relationship for the CaCO_3 deposition process in polycarbonate and MDPE foam substrates. Note the exponentially decaying behavior independent of the template and applied electric potential.

Appendix D: X-ray Diffraction

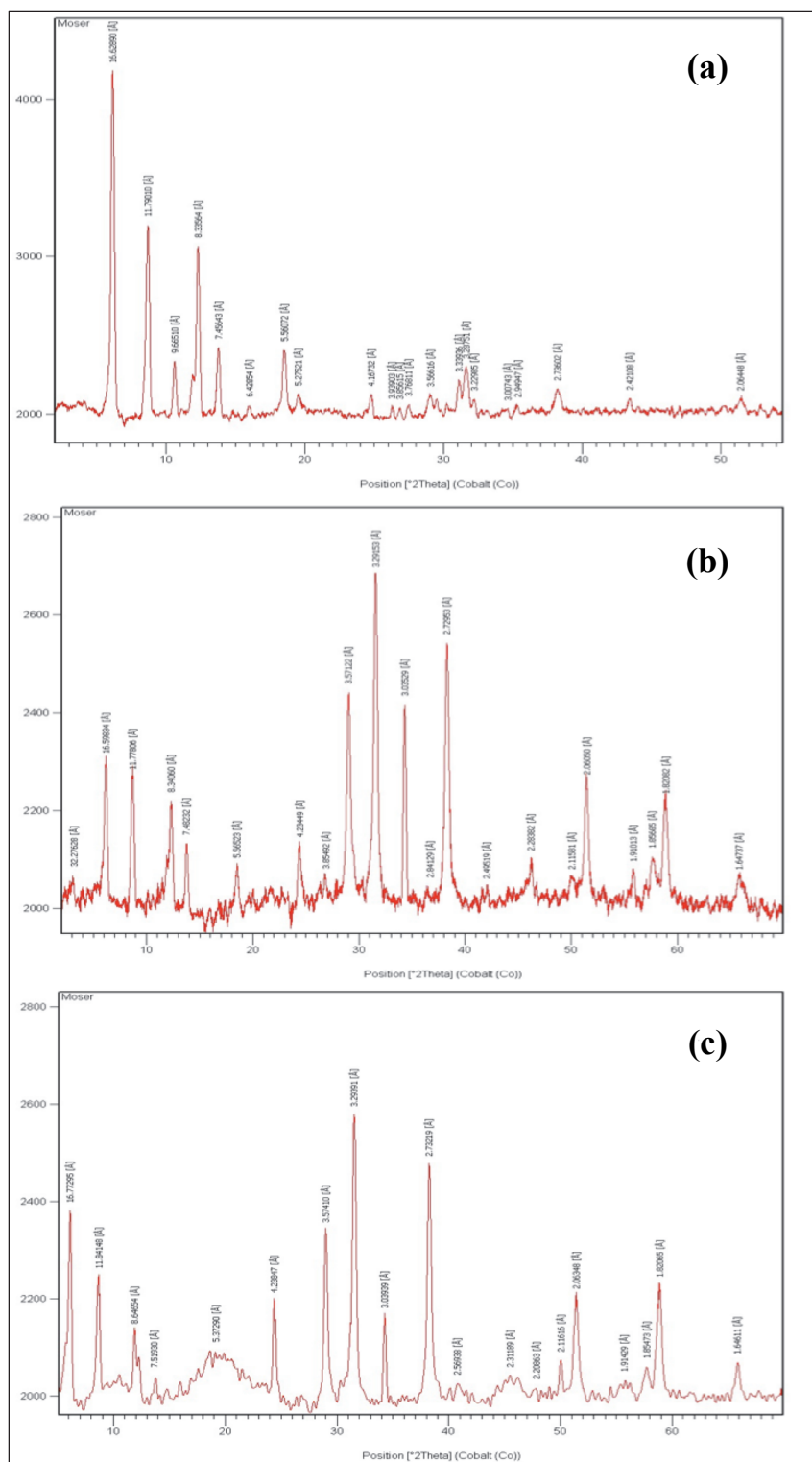


Figure D1. X-ray diffraction patterns for 5- (a), 10- (b), and (c) 20-V-3-hr specimens. The X-ray technique reveals the morphology-voltage/time relationship; higher applied cell potentials and shorter test durations resulted in an increase in the proportion of metastable phases such as vaterite and amorphous calcium carbonate.

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14. ABSTRACT Electromigration and electrodeposition techniques are ideal for synthesizing biomimetic and bio-inspired materials in predefined porous templates. Here, we demonstrate the utility of precipitating various polymorphs of calcium carbonate in three-dimensional templates. Applied potentials and times were varied and scanning electron microscopy and X-ray diffraction were used to determine polymorph formed and its morphology. It was found that higher applied potentials and shorter operating times resulting in the formation of metastable polymorphs of calcium carbonate (e.g., vaterite) that infilled the porous media. Results are essential for developing bio-inspired composite materials for various structural and medical applications.					
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